CHAPTER 4

RESULTS AND DISCUSSION

3.1 The Study of Equilibration Time.

The results of the study of the equilibration times for each semivolatile organic compound, i.e., ethylbenzene, chlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene and 1,2-dichlorobenzene obtained from the procedure in experimental section 3.5.1 are given in Tables 4.1 - 4.5. The graphs plotted the peak area (A_g) of each semivolatile organic compound against time are shown in the Figures 4.1 - 4.5. It is found that the equilibration time obtains from the study is 3 minutes for ethylbenzene, 5 minutes for chlorobenzene, 10 minutes for 1,3-dichlorobenzene and 1,4-dichlorobenzene, and 20 minutes for 1,2-dichlorobenzene. Therefore, the 30 minutes is chosen as the optimum equilibration time for the studied compounds and it is used for the entire studies to ensure that the system is in the equilibrium.

Table 4.1   The results of the effect of equilibration time
on the peak area of ethylbenzene.

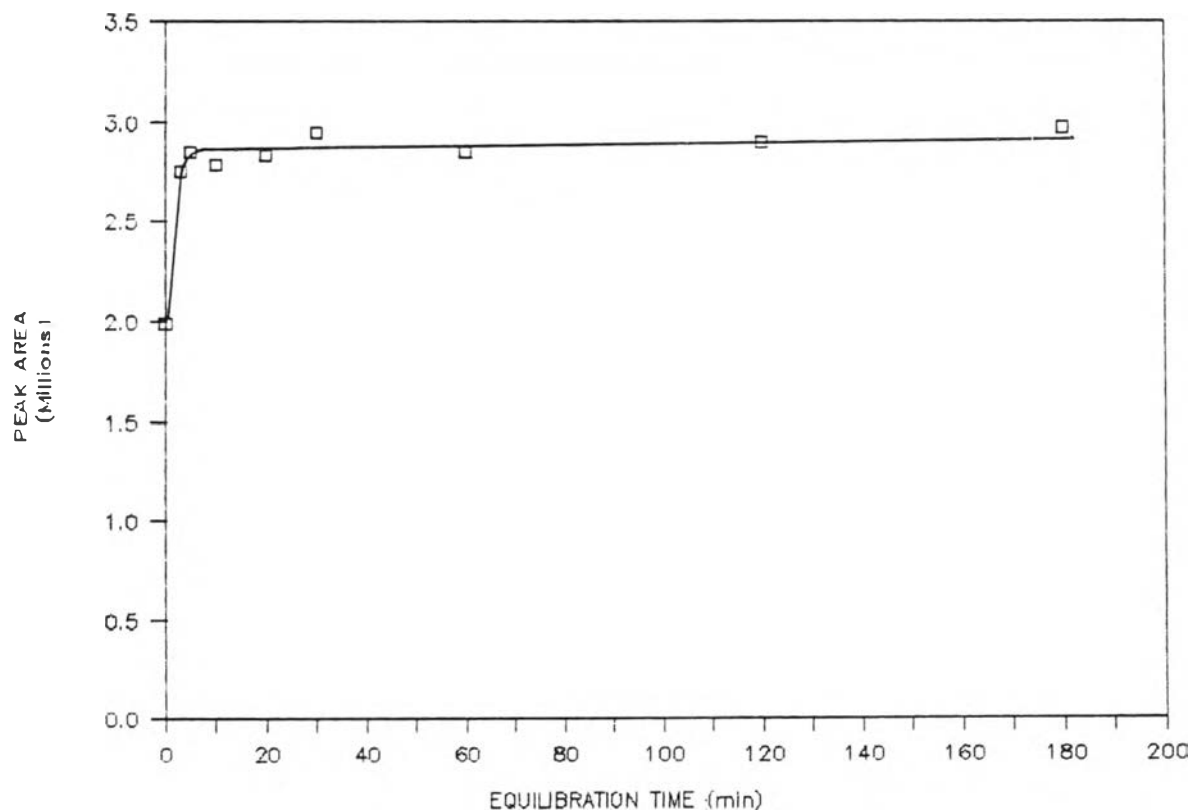| Time (min)	Peak area	% RSD
0	1986333	4.61
3	2748038	4.43
5	2851190	1.61
10	2783256	1.04
20	2833896	5.11
30	2944840	1.00
60	2847518	4.48
120	2896390	1.86
180	2970814	3.26

Triplicate analyses

Figure 4.1   The effect of equilibration time on the peak
area of ethylbenzene.

Table   4.2   The results of the effect of equilibration time

on the peak area of chlorobenzene.

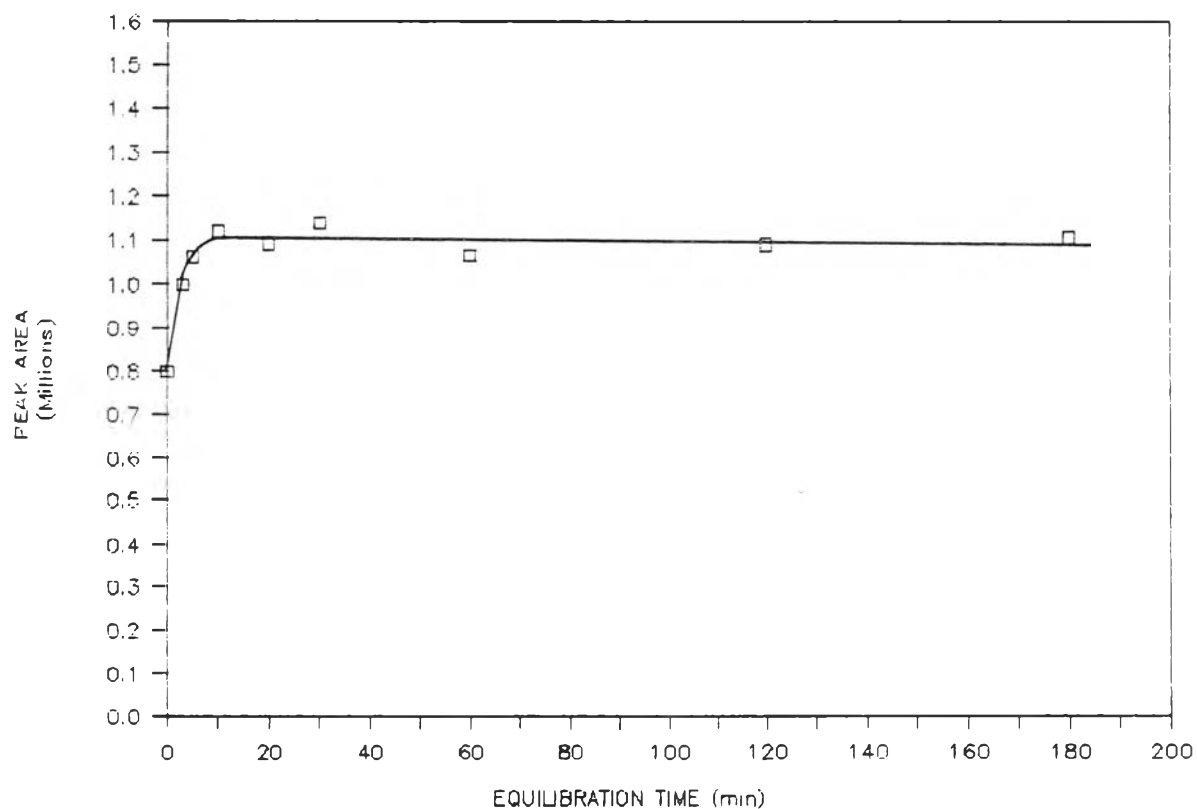| Time (min)	Peak area	% RSD
0	796217	5.39
3	997850	4.12
5	1061966	3.84
10	1117934	2.61
20	1092528	5.68
30	1139925	2.82
60	1065467	3.04
120	1088822	2.83
180	1104422	2.11

Triplicate analyses

Figure   4.2   The effect of equilibration time on the peak

area of chlorobenzene.

Table 4.3   The results of the effect of equilibration time

on   the peak area of 1,3-dichlorobenzene.

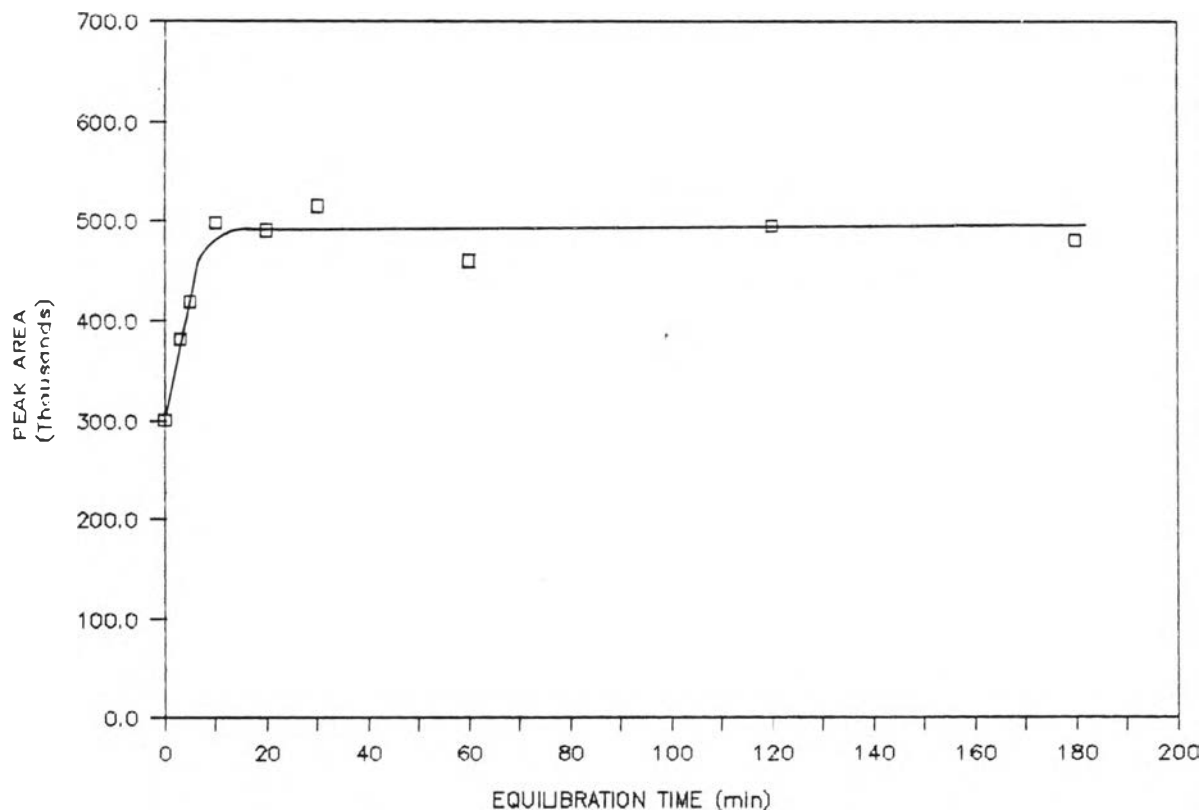| Time (min)	Peak area	% RSD
0	299573	11.73
3	381095	6.64
5	418328	12.54
10	497941	4.37
20	490613	2.39
30	514985	5.39
60	460204	7.75
120	495042	7.21
180	480704	6.07

Triplicate analyses

Figure   4.3   The effect of equilibration time on the peak

area of 1,3-dichlorobenzene.

Table 4.4   The results of the effect of equilibration time

on the peak area of 1,4-dichlorobenzene.

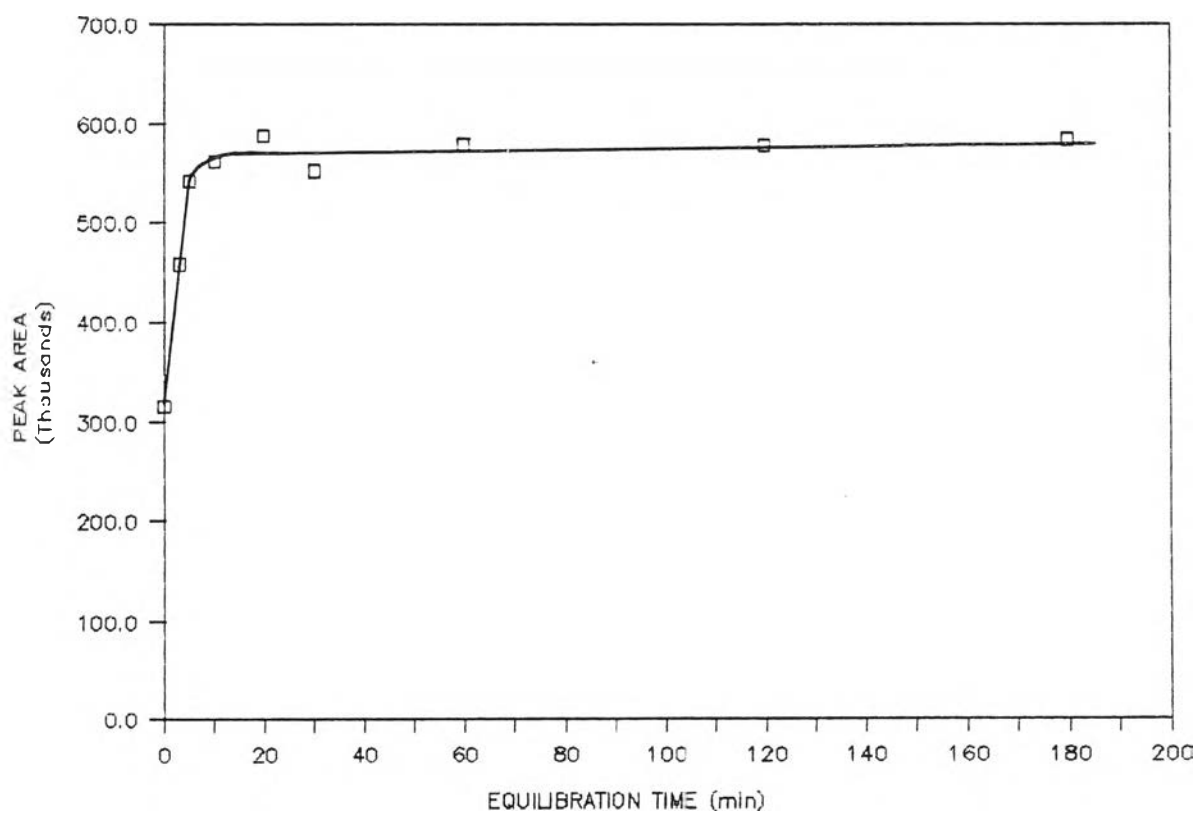| Time (min)	Peak area	% RSD
0	314895	6.71
3	458468	1.26
5	541429	6.38
10	561128	6.08
20	587252	3.96
30	552506	6.43
60	578528	2.21
120	577173	5.90
180	583756	4.20

Triplicate analyses

Figure   4.4   The effect of equilibration time on the peak

area of 1,4-dichlorobenzene.

Table 4.5   The results of the effect of equilibration time on

the peak area of 1,2-dichlorobenzene.

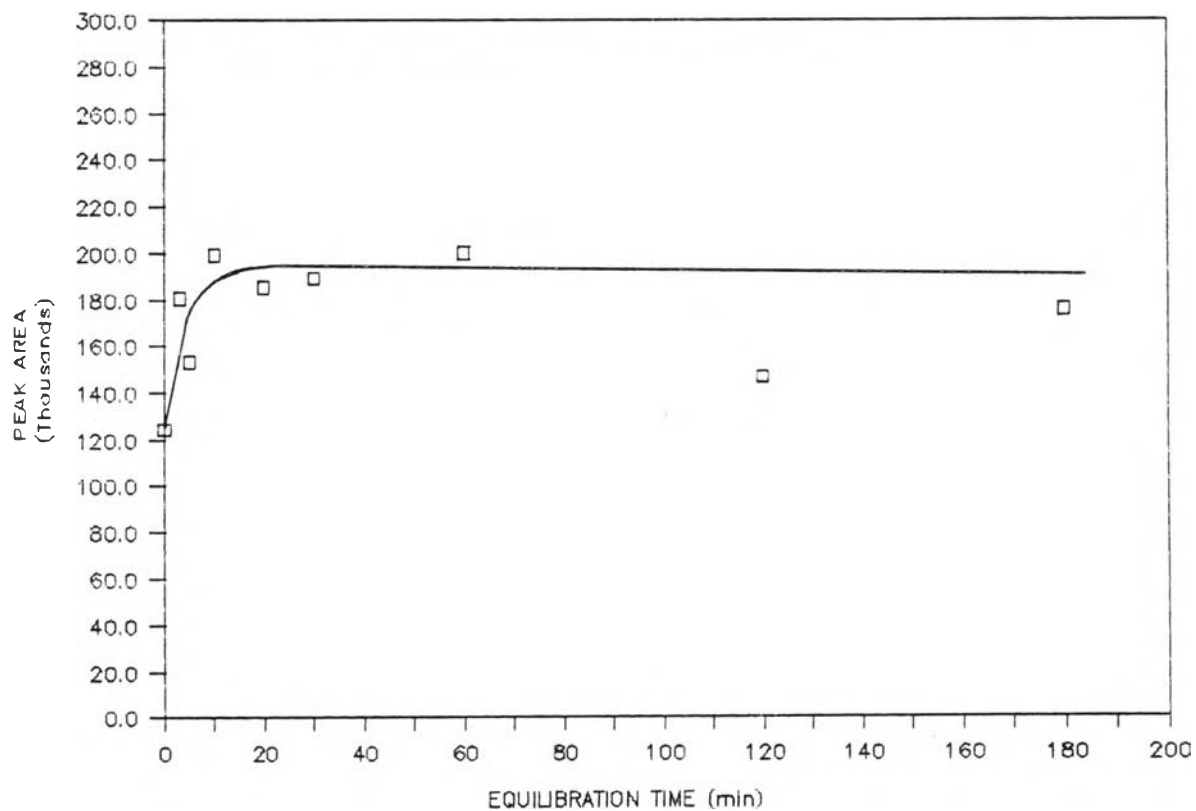| Time (min)	Peak area	% RSD
0	124173	4.44
3	180454	3.06
5	153451	2.20
10	199193	5.41
20	185317	10.09
30	189334	1.78
60	199850	3.66
120	146764	2.32
180	175698	1.30

Triplicate analyses

Figure   4.5   The effect of equilibration time on the peak

area of 1,2-dichlorobenzene.

3.2 The Study of Temperature

The effect of temperature on the distribution coefficient, K, of each semivolatile organic compound i.e., ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene was studied. The results of the study are presented in Table 4.6 and the graph showing the relationship of the distribution coefficient of each semivolatile organic compound with the temperature is in Figure 4.6 . It indicates that the distribution coefficient of each semivolatile organic compound decreases when the temperature of system increases. Hence, the temperature has the effect on the distribution coefficient of each compound and it can be explained by the fact that raising temperature will increase the vapor pressure of each compound and therefore, their solubility in the solution will be decreased as the concentration of each compound in the gas phase will be increased as the results shown in Table 4.6.

The result of the effect of the temperature including 30.0°, 40.0°, 50.0°, 60.0°, and 70.0° C on the sensitivity of each semivolatile organic compound is shown in Table 4.7. The graph plotted the sensitivity of each semivolatile organic compound against temperature is shown in Figure 4.7. It demonstrates that the temperature has the effect on the sensitivity of each semivolatile organic compound and therefore increasing temperature of the system will result in the enhancement of the sensitivity of the headspace analysis technique. According to the result in Table 4.7, it can be seen that the highest sensitivity of the headspace analysis technique is obtained at the temperature of 70.0 $^{\circ}$C which

is different from the temperature used in the study . However, at high temperature, the pressure in the system will be built up causing the leak of the components from the headspace sample vial. Moreover, the water vapor in the headspace gas will be increased resulting in the decrease in the detector response. Therefore, the temperature of 45.0 $^{\circ}$C giving a sufficient sensitivity for the determination of each semivolatile organic compound is chosen as an optimum temperature for use in the headspace analysis.

Table 4.6   The effect of temperature on the distribution
             coefficient and the equilibrium concentration
             of each semivolatile organic compound in gas phase.

Compound	Temperature (^{O}C)	K	Cg (ppb)
Ethylbenzene	30.0	3.74	97.70
	40.0	2.39	132.76
	50.0	1.55	171.33
	60.0	1.07	204.79
	70.0	0.59	253.51
Chlorobenzene	30.0	7.59	59.12
	40.0	4.87	84.67
	50.0	3.32	112.98
	60.0	2.13	151.36
	70.0	1.25	201.17
1,3-Dichlorobenzene	30.0	14.29	32.03
	40.0	8.26	51.82
	50.0	4.97	78.64
	60.0	3.24	108.33
	70.0	2.38	132.74
1,4-Dichlorobenzene	30.0	16.45	28.08
	40.0	9.64	45.41
	50.0	5.95	68.08
	60.0	4.06	91.66
	70.0	2.82	118.71
1,2-Dichlorobenzene	30.0	24.29	19.61
	40.0	15.23	30.10
	50.0	10.04	43.72
	60.0	6.41	64.29
	70.0	4.28	88.21

Triplicate analyses

Table 4.7   The results of the effect of temperature on the

sensitivity of each semivolatlie organic compound.

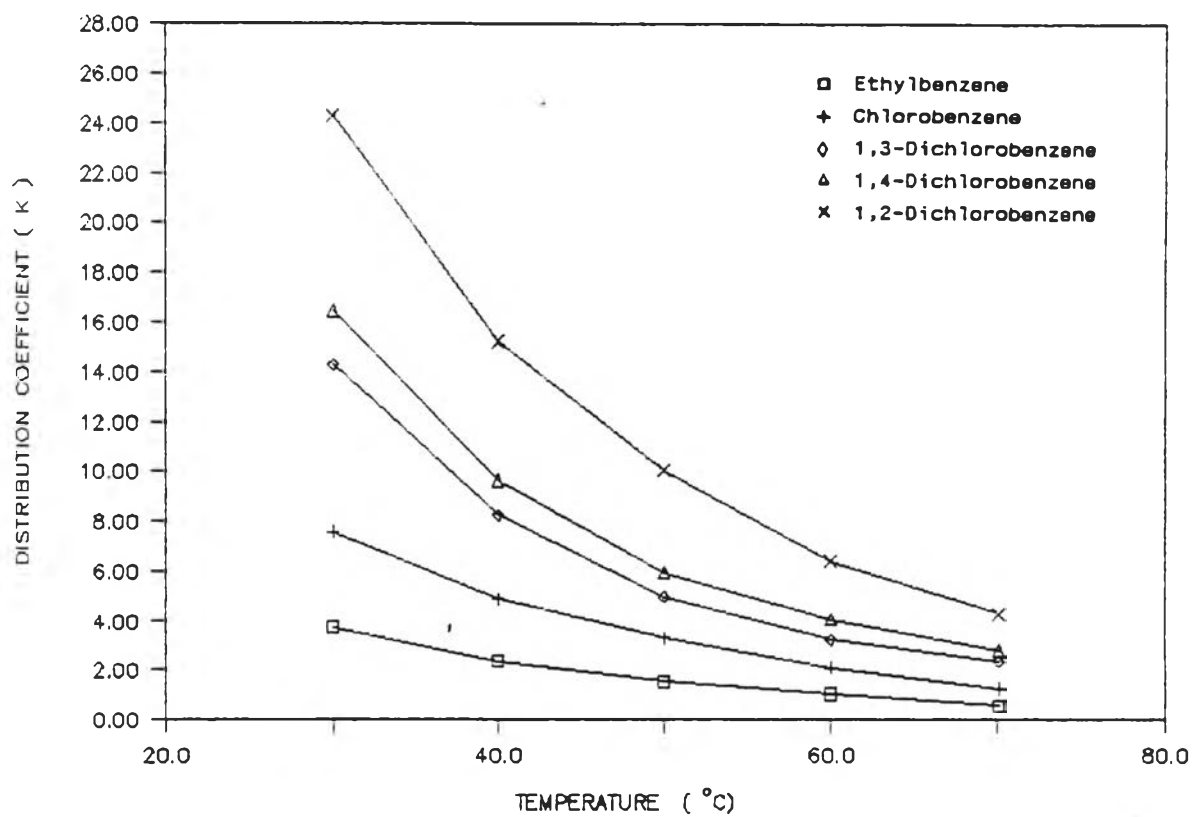| Compound	Temperature (^{o}C)	Sensitivity
Ethylbenzene	30.0	4492
	40.0	6112
	50.0	7895
	60.0	9441
	70.0	11693
Chlorobenzene	30.0	1596
	40.0	2283
	50.0	3045
	60.0	4077
	70.0	5416
1,3-Dichlorobenzene	30.0	606
	40.0	968
	50.0	1458
	60.0	2000
	70.0	2446
1,4-Dichlorobenzene	30.0	697
	40.0	1101
	50.0	1629
	60.0	2177
	70.0	2807
1,2-Dichlorobenzene	30.0	396
	40.0	619
	50.0	908
	60.0	1344
	70.0	1852

Triplicate analyses

Figure 4.6 The effect of temperature on the distribution coefficient of each semivolatile organic compound.
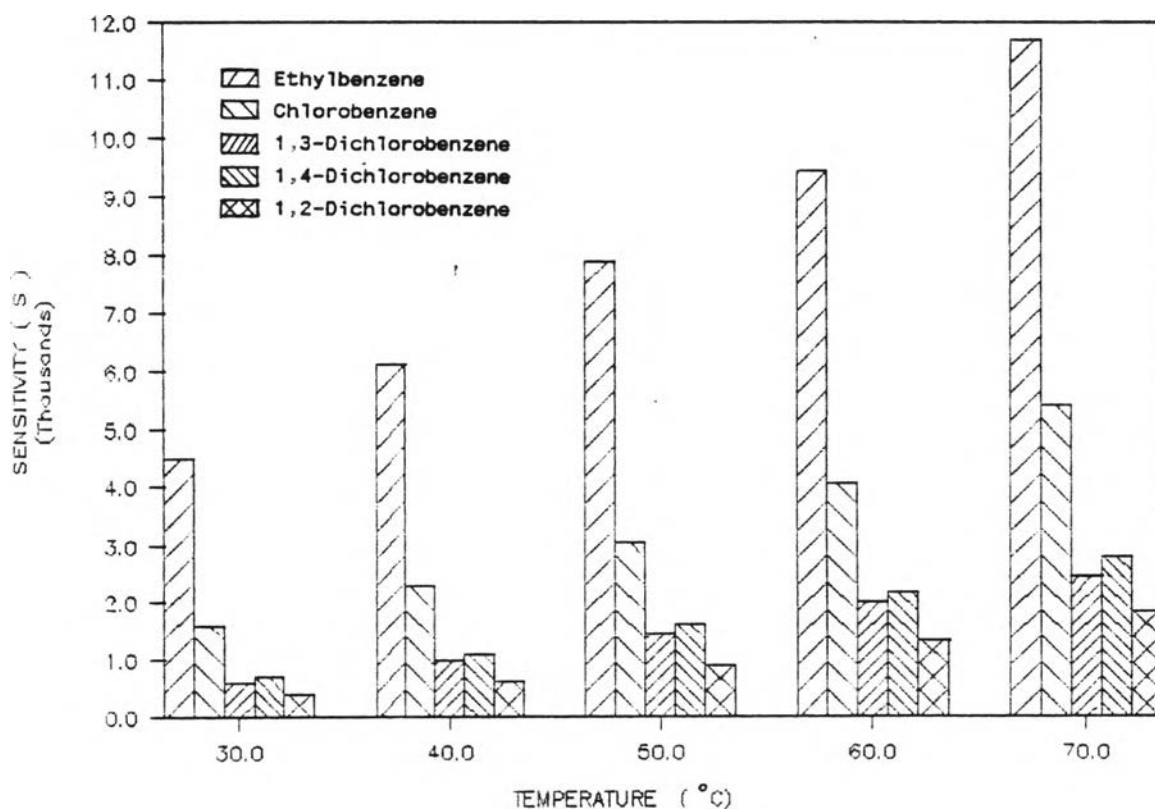

Figure 4.7 The effect of temperature on the sensitivity of each semivolatile organic compound.

3.3 The Study of Liquid to Gas Phase Ratio

The factor effecting the sensitivity of headspace analysis technique is also the liquid to gas phase ratio. The selection of the correct liquid to gas phase ratio will result in highest sensitivity and accurate analysis. Therefore, its effect on the distribution coefficient and the sensitivity of each semivolatile organic compound is studied so as to determine the optimum liquid to gas phase ratio for the headspace analysis.

The results of liquid to gas phase ratio having the effect on the distribution coefficient and the sensitivity of each semivolatile organic compound i.e., ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene are presented in Tables 4.8 - 4.9, respectively. The graphs plotted the distribution coefficient, K, and the sensitivity, S, of each semivolatile organic compound against the liquid to gas phase ratio are shown in Figure 4.8 and Figures 4.9 - 4.13, respectively. It is shown that the distribution coefficient of each semivolatile organic compound decreases when the value of liquid to gas phase ratio increases. The decrease in the value of distribution coefficient will continue until the ratio of V_l/V_g reaches 25:35 and it will remain constant up to higher phase ratios. Therefore, the sensitivity of each semivolatile organic compound remains slightly different in the liquid to gas phase ratios ranges from 25:35 to 50:10 as seen in Figures 4.10 through 4.13, except for ethylbenzene, as shown in Figure 4.9, and the reasons of this is that the polarity of ethylbenzene is less than the other studied

Table 4.8   The effect of liquid to gas phase ratio on equilibrium concentration in gas phase and the distribution coefficient of each semivolatile organic compound.

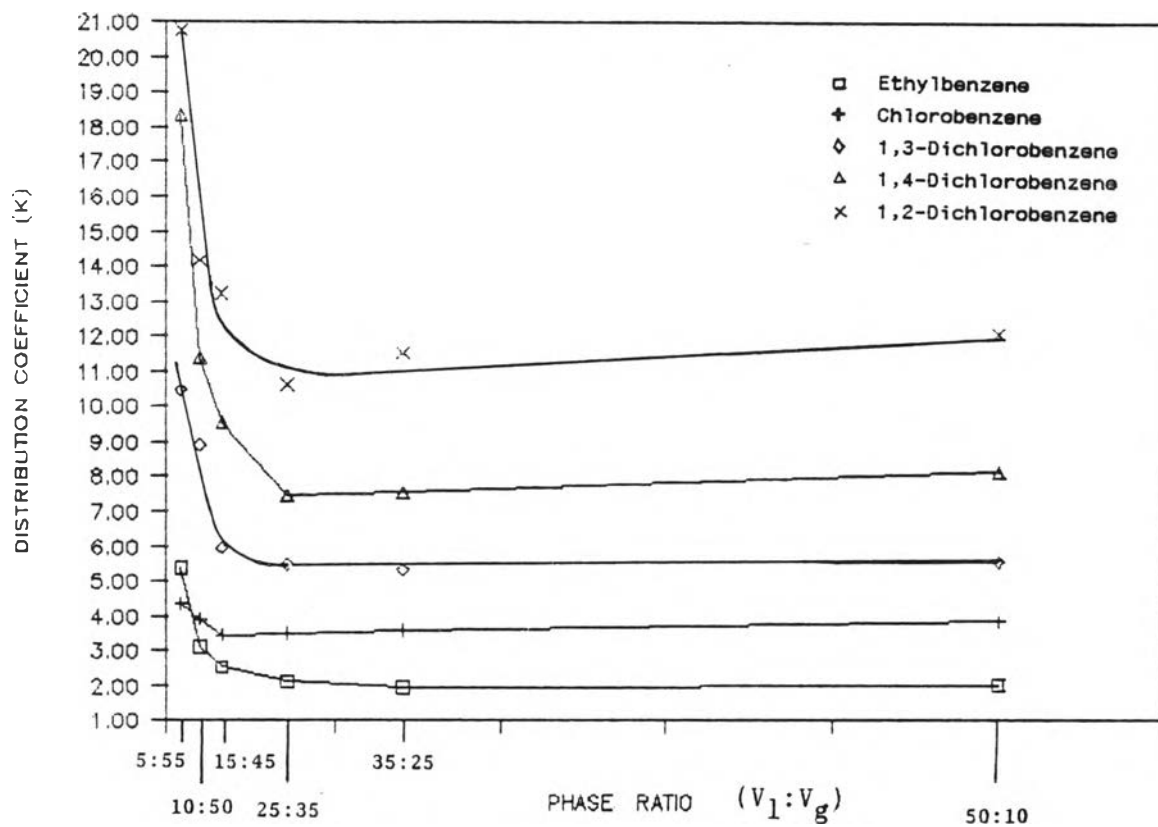| Compound	$V_l:V_g$	C_g (ppb)	K
Ethylbenzene	50:10	227.74	2.01
	35:25	188.82	1.95
	25:35	143.32	2.11
	15:45	91.26	2.54
	10:50	61.73	3.10
	5:55	30.82	5.38
Chlorobenzene	50:10	131.70	3.83
	35:25	124.18	3.56
	25:35	109.22	3.48
	15:45	82.88	3.45
	10:50	59.52	3.91
	5:55	34.78	4.34
1,3-Dichlorobenzene	50:10	87.45	5.56
	35:25	83.16	5.31
	25:35	72.98	5.48
	15:45	55.93	5.95
	10:50	35.97	8.90
	5:55	23.24	10.46
1,4-Dichlorobenzene	50:10	59.93	8.14
	35:25	60.63	7.54
	25:35	56.65	7.45
	15:45	40.47	9.51
	10:50	30.59	11.38
	5:55	17.16	18.33
1,2-Dichlorobenzene	50:10	40.77	12.09
	35:25	40.88	11.53
	25:35	41.75	10.62
	15:45	30.94	13.22
	10:50	26.11	14.16
	5:55	15.82	20.74

Triplicate analyses

Figure 4.8   The distribution coefficient of each semivolatile

organic compound versus liquid to gas phase   ratio

Table   4.9   The effects of liquid to gas phase ratio on the
                sensitivity of each semivolatile organic compound.

Compound[*]	V_l:V_g	Sensitivity	Relative sensitivity
ETB	50:10	10317	7.50
	35:25	8550	6.21
	25:35	6484	4.71
	15:45	4121	2.99
	10:50	2780	2.02
	5:55	1376	1.00
CB	50:10	3667	3.84
	35:25	3457	3.62
	25:35	3038	3.18
	15:45	2302	2.41
	10:50	1648	1.72
	5:55	956	1.00
mCB	50:10	1619	3.63
	35:25	1540	3.46
	25:35	1351	3.03
	15:45	1043	2.34
	10:50	678	1.52
	5:55	446	1.00
pCB	50:10	1439	3.25
	35:25	1455	3.29
	25:35	1359	3.07
	15:45	986	2.23
	10:50	756	1.71
	5:55	443	1.00
oCB	50:10	845	2.68
	35:25	847	2.68
	25:35	866	2.74
	15:45	636	2.02
	10:50	534	1.69
	5:55	316	1.00

Triplicate analyses

[*] ETB = Ethylbenzene, CB = Chlorobenzene, mCB = 1,3-Dichlorobenzene

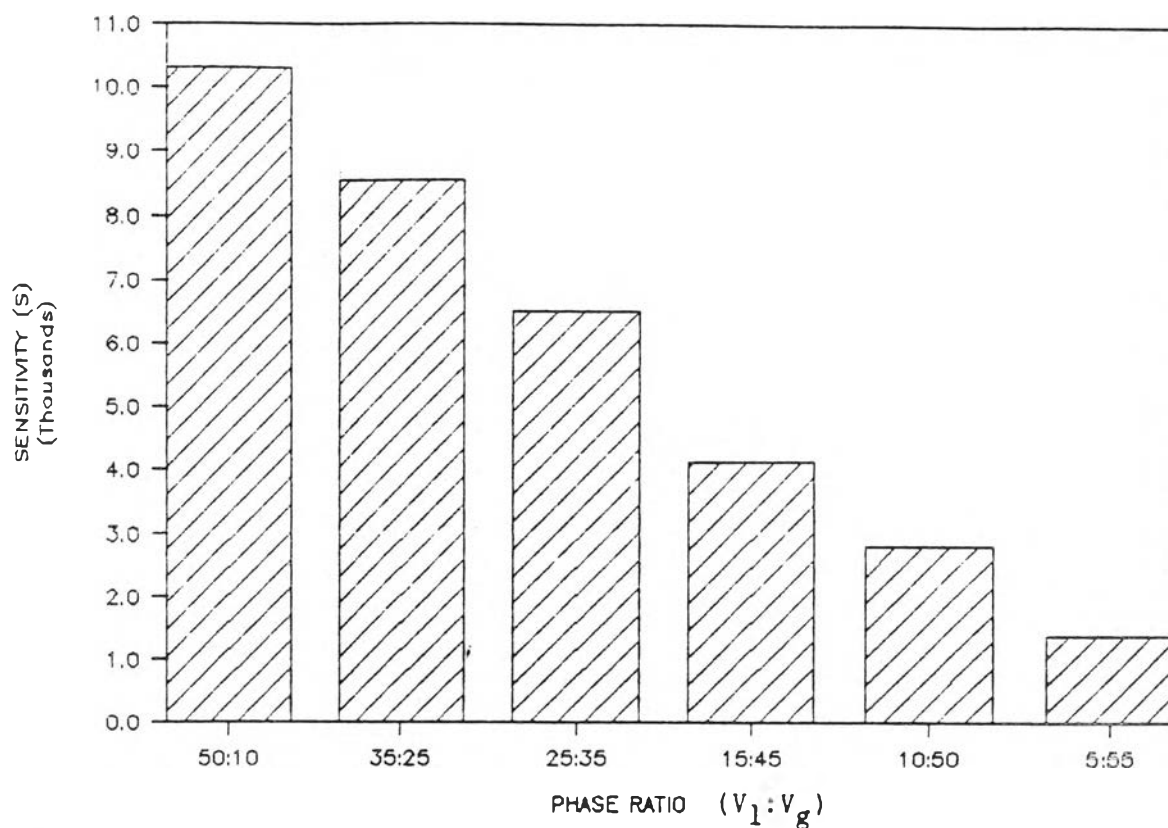pCB = 1,4-Dichlorobenzene, oCB = 1,2-Dichlorobenzene

Figure 4.9   The effect of liquid to gas phase ratio on the sensitivity of ethylbenzene.
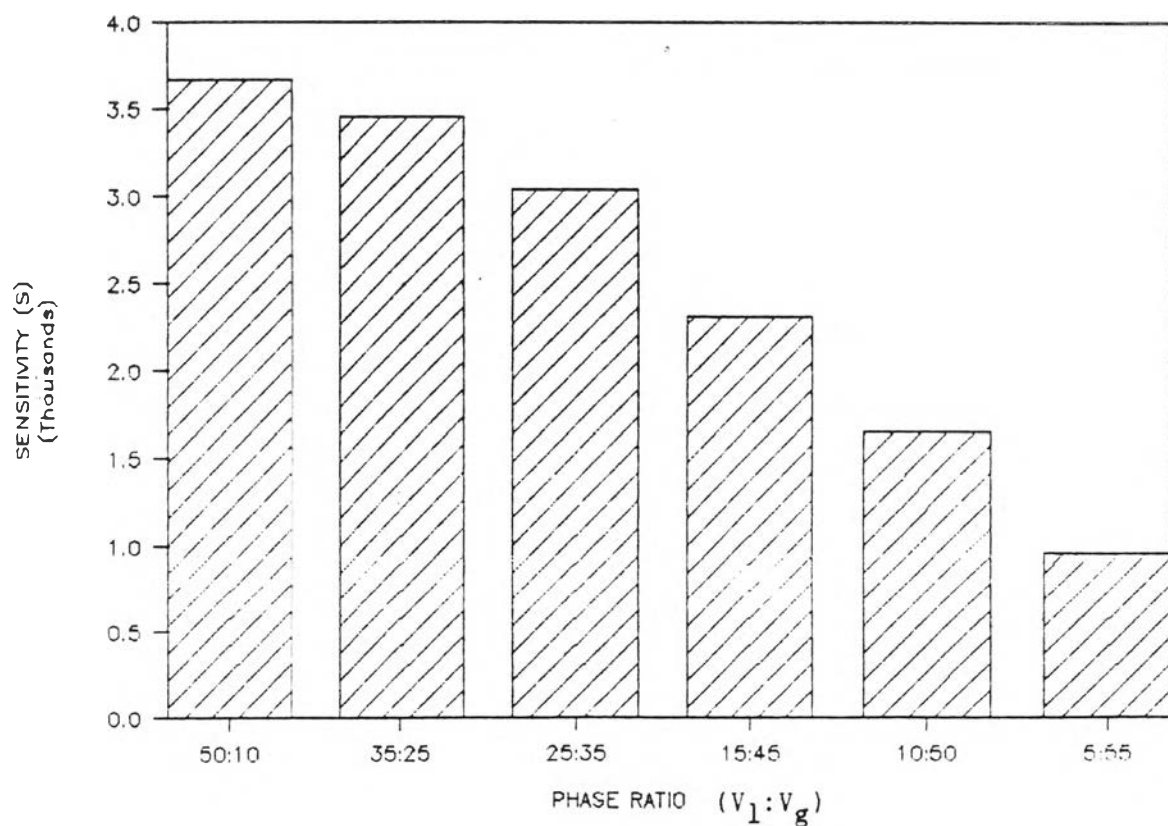

Figure 4.10   The effect of liquid to gas phase ratio on the sensitivity of chlorobenzene.
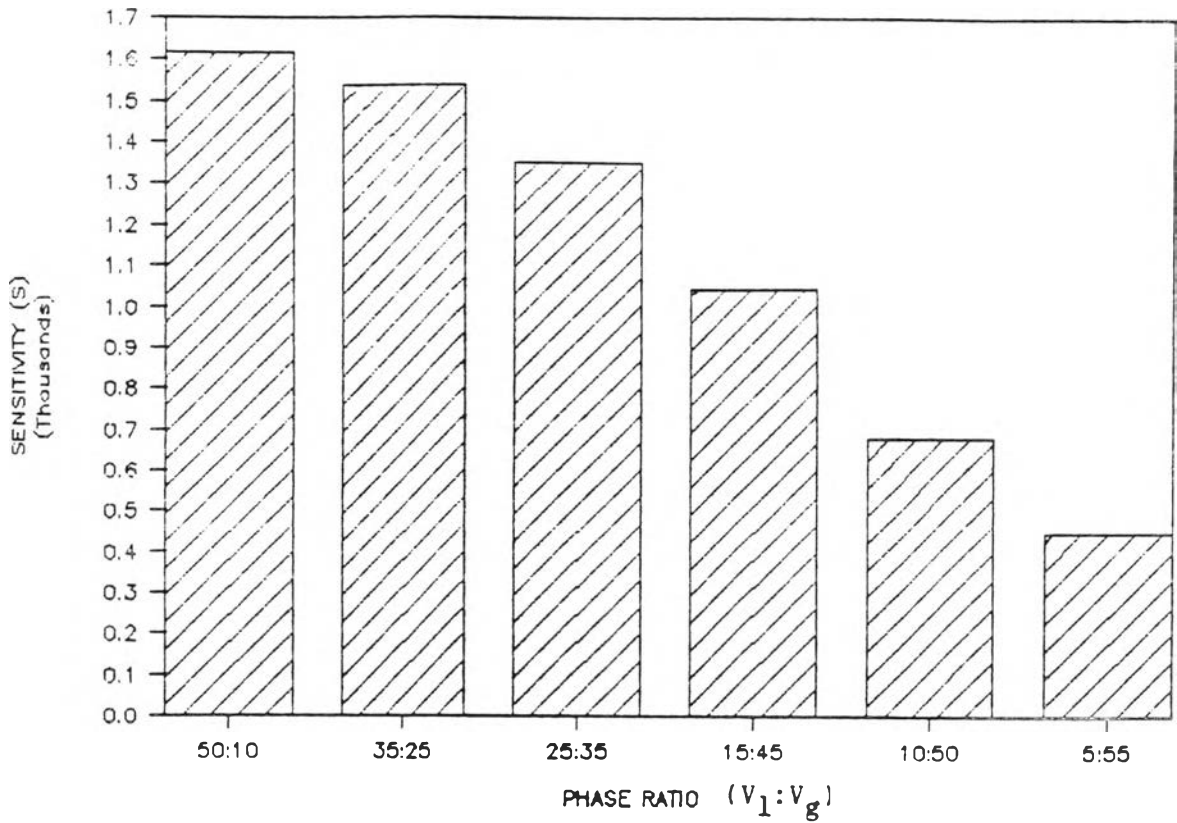
Figure 4.11   The effect of liquid to gas phase ratio on the sensitivity of 1,3-dichlorobenzene.
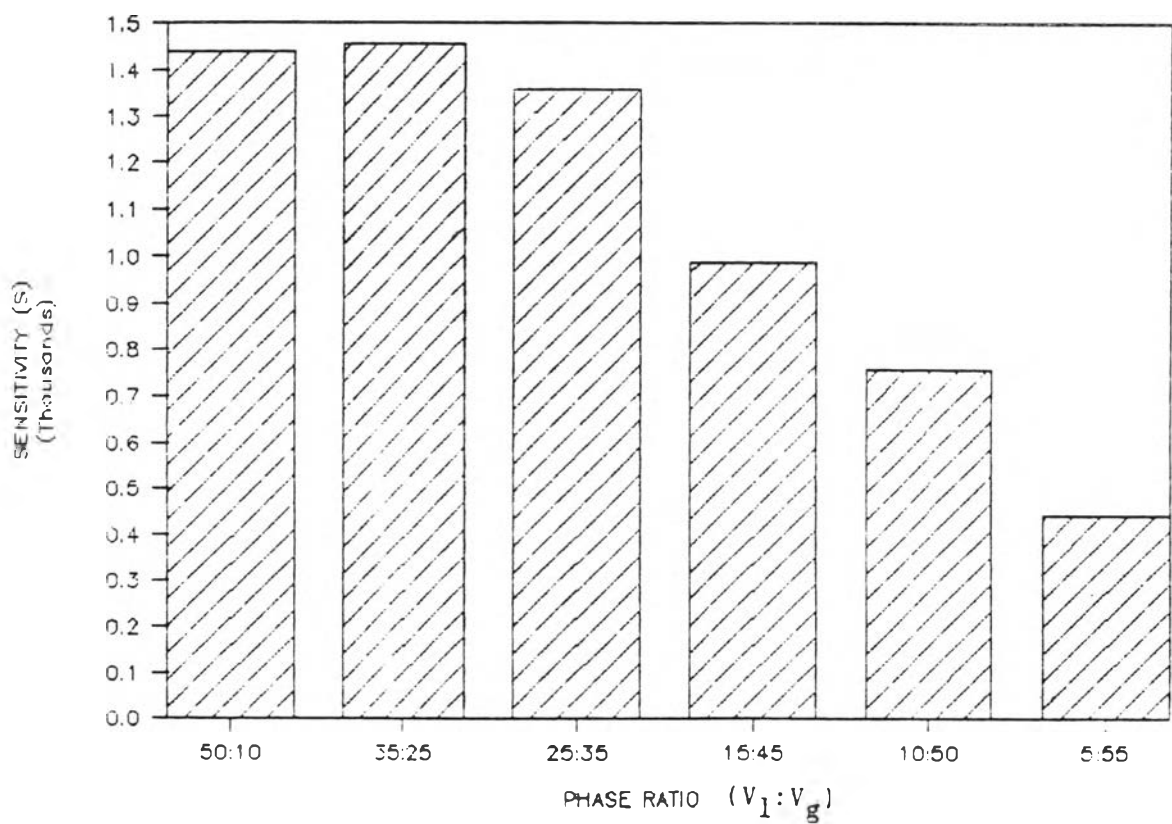

Figure 4.12   The effect of liquid to gas phase ratio on the sensitivity of 1,4-dichlorobenzene.
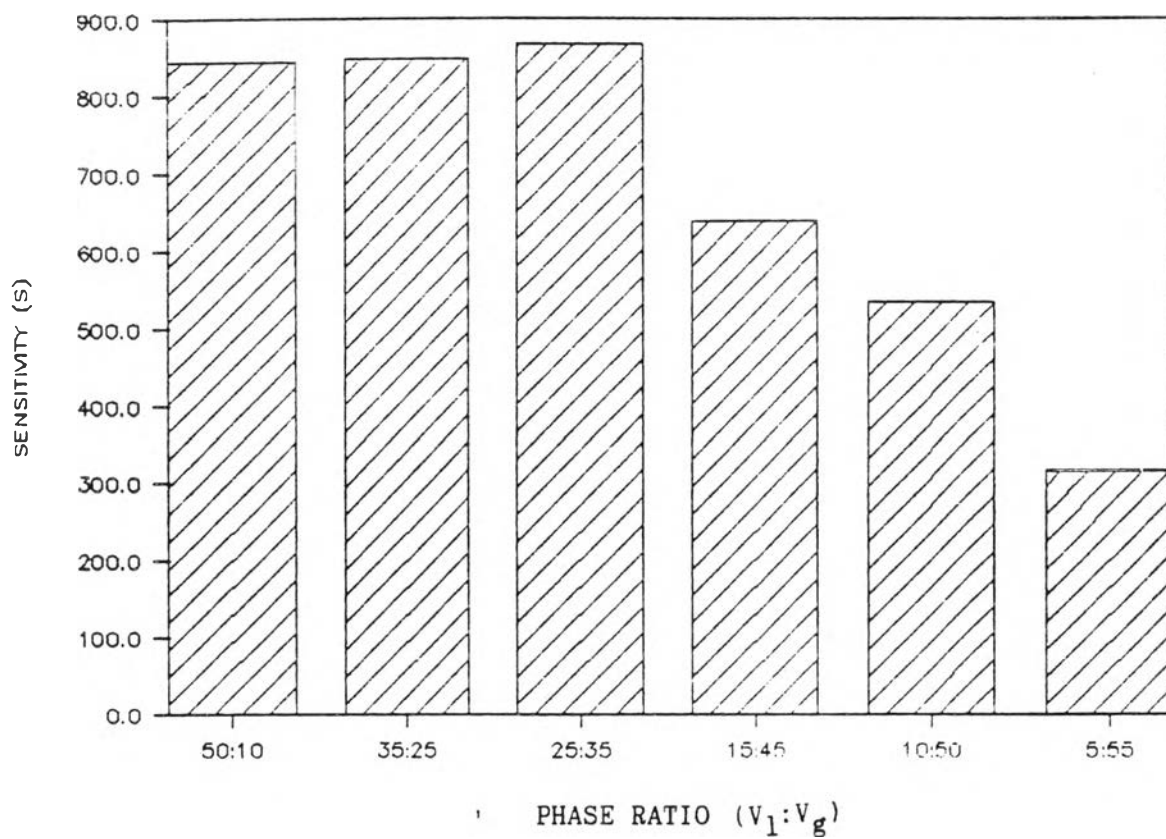
Figure 4.13   The effect of liquid to gas phase   ratio   on the sensitivity of 1,2-dichlorobenzene.

compounds. Hence, the liquid to gas phase ratio of 25:35 is selected as suitable ratio for a headspace analysis due to the sensitivity is not different from another phase ratios as shown in Figures 4.10 through 4.13 and increasing phase ratio will also result in the error of an analysis (22).

3.4 The Study of Injection Volume

The peak area which is corresponding to the sensitivity of the headspace analysis can be increased by means of the increasing of the injection volume of the headspace gas. Therefore, the effects of the sample size or injection volume of the headspace gas on the peak area and the sensitivity of each semivolatile organic compound i.e., ethylbenzene, chlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene and 1,2-dichlorobenzene are studied. The results of the study are presented in Table 4.10 and the graphs plotted the peak area and the sensitivity against the injection volume are shown in Figures 4.14 and 4.15, respectively. It is found that the peak area of each semivolatile organic compound increases linearly with the injection volume as shown in Figure 4.14 and the maximum sensitivity of each semivolatile organic compound is found at the highest injection volume as seen in Figure 4.15 . The reason to select 2.00 mL as the optimum injection volume is that 1,3-dichlorobenzene and 1,4-dichlorobenzene will not be able to separate from each other by increasing the sample size or injection volume as seen from the chromatogram in Figure 4.18 . Therefore, the injection volume of 2.00 mL is used as the injection volume for the headspace analysis.

Table 4.10   The results of the effect of injection volume on

the peak area and the sensitivity of each semivolatile

organic compound.

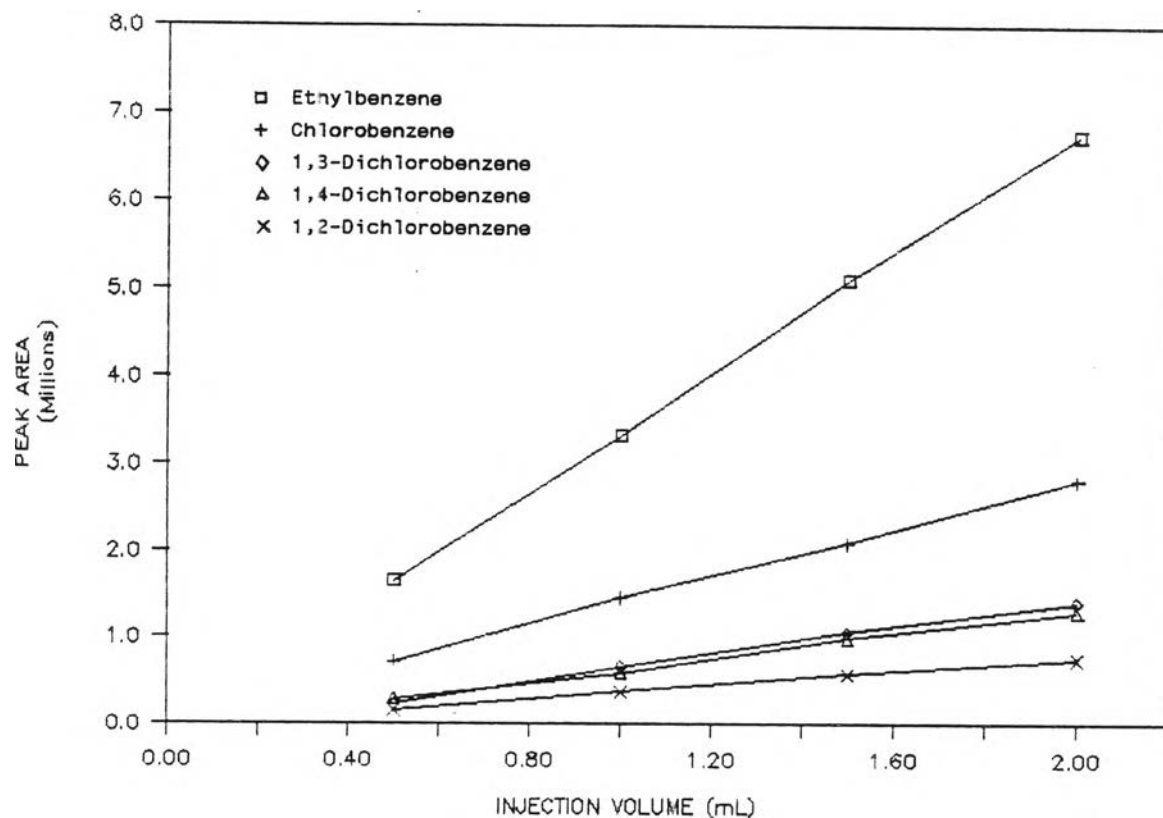| Compound	Injection volume (mL)	Peak area	Sensitivity	% RSD
Ethylbenzene	0.50	1645452	3279	3.58
	1.00	3311178	6600	3.65
	1.50	5094905	10155	1.50
	2.00	6749663	13454	0.97
Chlorobenzene	0.50	715445	1347	2.45
	1.00	1454750	2740	2.76
	1.50	2076236	3910	2.49
	2.00	2804197	5282	3.50
1,3-Dichlorobenzene	0.50	225001	450	13.93
	1.00	662476	1324	19.15
	1.50	1058393	2116	7.38
	2.00	1402253	2804	5.08
1,4-Dichlorobenzene	0.50	286175	572	2.51
	1.00	588530	1177	6.62
	1.50	986936	1973	4.39
	2.00	1294502	2589	2.54
1,2-Dichlorobenzene	0.50	152611	305	4.48
	1.00	367966	735	3.02
	1.50	576937	1153	4.29
	2.00	750273	1500	4.37

Triplicate analyses

Figure 4.14   The relationship between the peak area of each
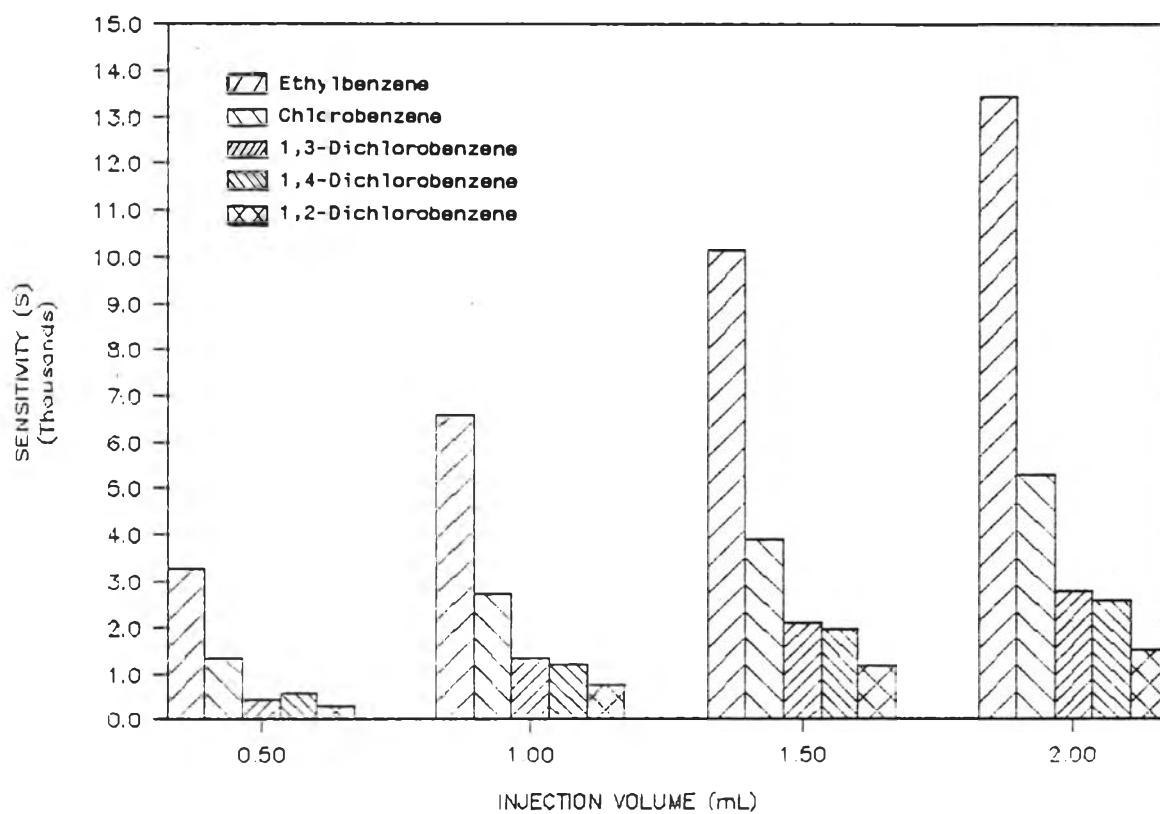semivolatile organic compound and injection volume.

Figure 4.15   The effect of injection volume on the sensitivity
of each semivolatile organic compound.

4.5 Salting Out Effect in Single Component Solution

The effect of adding salt i.e., 10.00 g of sodium chloride
and 10.00 g of anhydrous sodium sulfate on the percent recovery,
%E, of each semivolatile organic compound, i.e., ethylbenzene,
chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-
dichlorobenzene is studied at two concentration levels i.e., 50 ppb
and 500 ppb in single component solution. The results of the study
are shown in Table 4.11 (a) and Table 4.11 (b). The graphs
correlated to these results are shown in Figure 4.16 (a) and Figure
4.16 (b).

It is found that the percent recovery, %E, of each
semivolatile organic compound in single component solutions ranges
from 9.57-47.56% with 2.04-7.52% %RSD for 50 ppb solutions and from
12.60-42.98 % with 1.28-6.58% %RSD for 500 ppb solutions for the
solution without any salt, from 42.32-79.30 % with 1.66-10.01 % %RSD
for 50 ppb solutions and from 44.35-74.11 % with 1.90-8.79% %RSD for
500 ppb solutions for adding 10.00 g of sodium chloride into the
solutions, from 54.87-87.04 % with 0.97-9.39 % %RSD for 50 ppb
solutions and from 56.61-86.90 % with 1.79-7.81 % %RSD for 500 ppb
solutions for adding 10.00 g of anhydrous sodium sulfate into the
solutions. This means that adding sodium sulfate or sodium chloride
into the solutions results in the increase in the percent recovery
of each semivolatile organic compound. However, adding anhydrous
sodium sulfate yields the percent recovery of each semivolatile
organic compound higher than sodium chloride do. Therefore, the
percent recovery of each semivolatile organic compound will be

Table 4.11   The results of salting out effect on percent recovery

of each semivolatile organic compound   in single

component solution.

(a)   50 ppb standard solution

| Compound	Salt	K	% E	%RSD
Ethylbenzene	No salt	1.57	47.56	2.67
	NaCl	0.29	79.30	1.66
	Na_2SO_4	0.18	87.04	4.86
Dichlorobenzene	No salt	3.40	29.16	3.51
	NaCl	0.60	64.52	5.99
	Na_2SO_4	0.21	85.59	2.60
1,3-Dichlorobenzene	No salt	4.31	24.67	2.04
	NaCl	0.78	59.13	5.07
	Na_2SO_4	0.49	72.55	9.39
1,4-Dichlorobenzene	No salt	8.13	14.98	3.70
	NaCl	1.51	42.32	3.16
	Na_2SO_4	1.04	54.87	0.97
1,2-Dichlorobenzene	No salt	13.60	9.57	7.52
	NaCl	1.36	45.25	10.01
	Na_2SO_4	1.05	54.97	8.55

Triplicate analyses
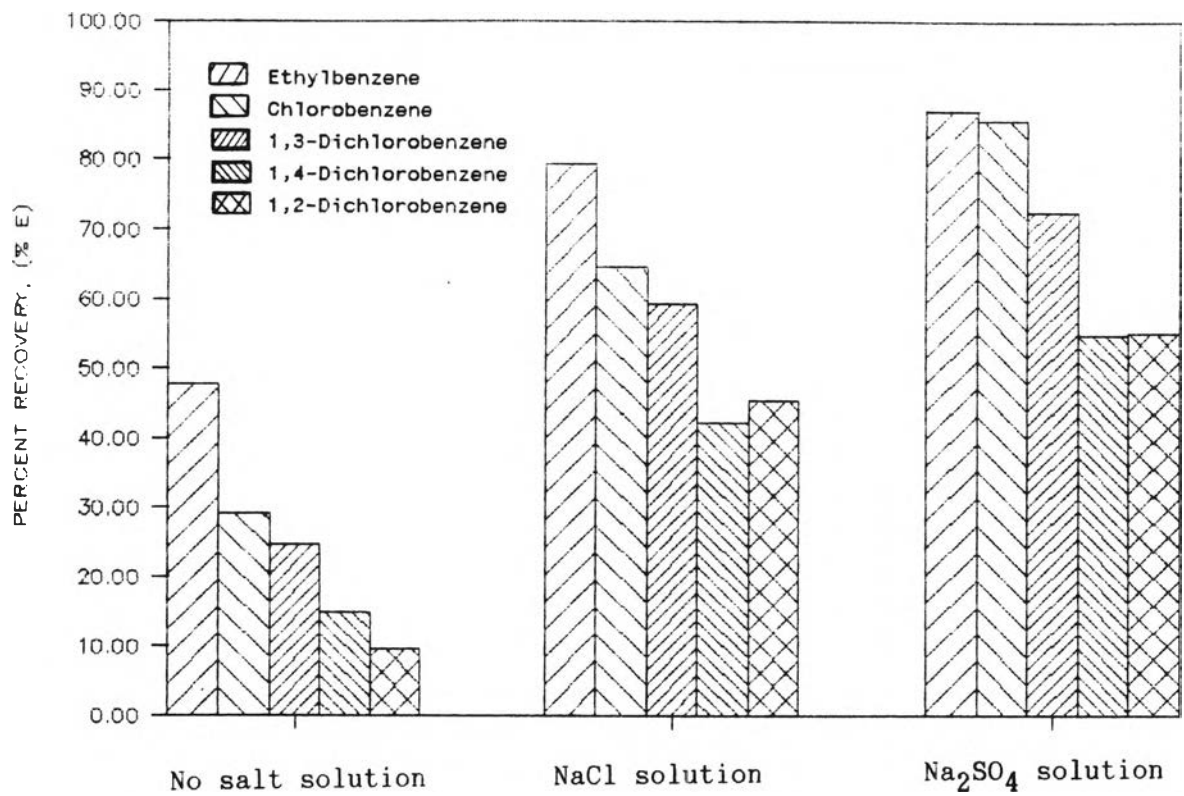
Figure 4.16 (a)   The effect of salting out on percent recovery of
each semivolatile organic compound at 50 ppb
in single component solution.

Table 4.11   The results of salting out effect on percent recovery
of each semivolatile organic compounds in single
component solution.

(b)   500 ppb standard solution

| Compound	Salt	K	% E	%RSD
Ethylbenzene	No salt	1.84	42.99	3.01
	NaCl	0.40	74.11	8.79
	Na$_2$SO$_4$	0.20	85.44	2.98
Chlorobenzene	No salt	3.45	28.82	1.28
	NaCl	0.55	67.43	1.90
	Na$_2$SO$_4$	0.19	86.90	1.80
1,3-Dichlorobenzene	No salt	4.18	25.03	3.02
	NaCl	0.69	61.09	8.14
	Na$_2$SO$_4$	0.45	73.63	2.81
1,4-Dichlorobenzene	No salt	6.93	17.02	6.58
	NaCl	1.20	48.43	2.52
	Na$_2$SO$_4$	0.84	60.03	1.79
1,2-Dichlorobenzene	No salt	19.79	12.60	1.30
	NaCl	1.43	44.35	2.92
	Na$_2$SO$_4$	0.98	56.61	7.81

Triplicate analyses
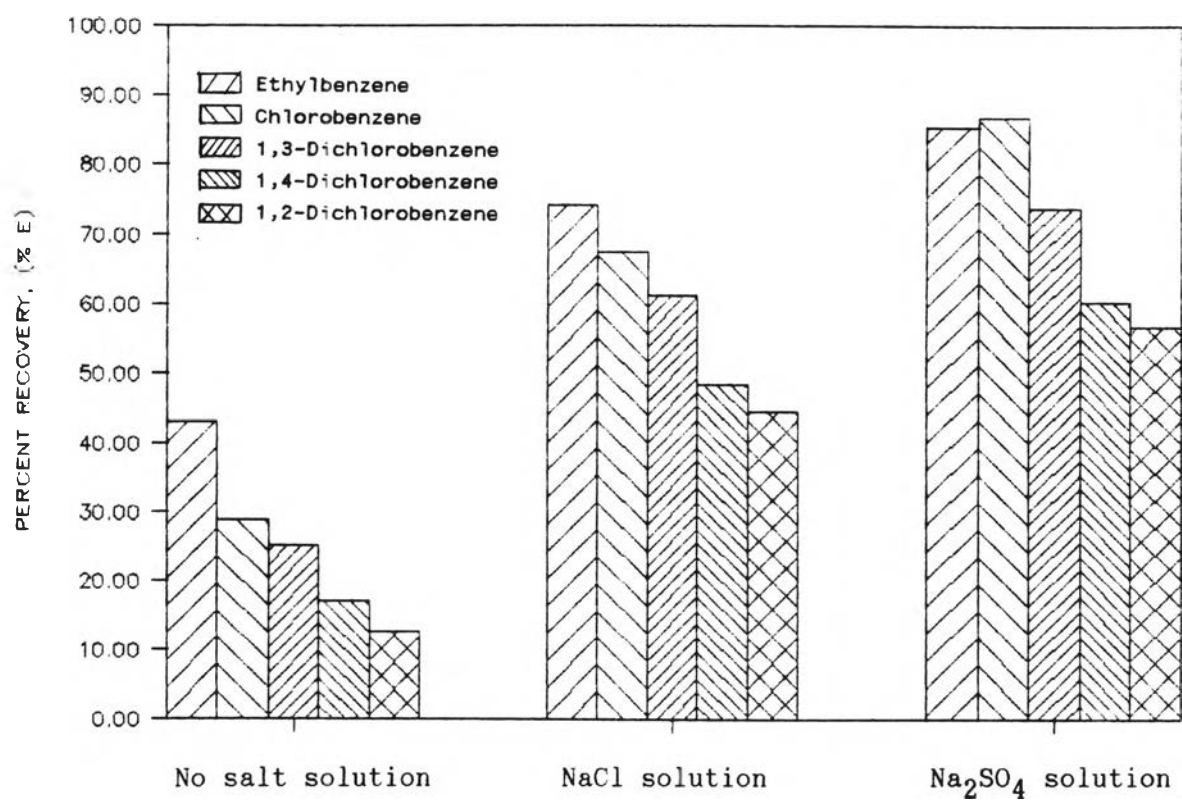
Figure 4.16 (b) The effect of salting out on percent recovery of
each semivolatile organic compound at 500 ppb
in single component solution.

increased as in the following order of adding salt into the solutions : nosalt, NaCl, and anhydrous Na_2SO_4. The reason of this is that adding anhydrous sodium sulfate into a solution yields the higher ionic strength than the sodium chloride and nonsalting out do.

4.6 The Salting Out Effect in Mixture Solution

The results of adding salts, i.e., 10.00 g of sodium chloride, and 10.00 g of anhydrous sodium sulfate on the percent recovery, %E, of each semivolatile organic compound, i.e., ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene at two concentration levels i.e., 50 ppb and 500 ppb of mixture in aqueous solution are shown in Tables 4.12(a) through 4.12 (b) and Figures 4.17 (a) through 4.17(b).

It is found that the percent recovery, %E, of each semivolatile organic compound in mixture solutions ranges from 15.44-47.35 % with 1.00-3.09 % %RSD for 50 ppb solutions and from 14.43-45.24 % with 0.82-2.67 % %RSD for 500 ppb solutions for nosalt, from 45.33-78.08 % with 1.75-3.85 % %RSD for 50 ppb solutions and from 42.10-76.80 % with 0.43-3.93 % %RSD for 500 ppb solutions for adding 10.00 g of sodium chloride into the solutions, from 57.45-91.51 % with 0.77-4.46 % %RSD for 50 ppb solutions and from 53.30-87.24 % with 3.81-10.62 % %RSD for 500 ppb solutions for adding 10.00 g of anhydrous sodium sulfate into the solutions. The salting out effect on the percent recovery in the single component solutions and mixture solutions are similar and adding anhydrous

sodium sulfate into the solutions gives the highest percent recovery for each semivolatile organic compound. Therefore, the anhydrous sodium sulfate is considered as the suitable salt which can be used to increase the percent recovery of each semivolatile organic compound in both single component and mixture solutions. Thus, the anhydrous sodium sulfate is chosen as the appropriate salt for the headspace analysis technique.

Table 4.12   The results of salting out effect on percent recovery of each semivolatile organic compound in mixture solution.

(a)   50 ppb standard solution

| Compound	Salt	K	% E	%RSD
Ethylbenzene	No salt	1.58	47.35	1.40
	NaCl	0.32	78.08	1.75
	Na_2SO_4	0.17	88.14	0.77
Chlorobenzene	No salt	2.65	34.88	1.00
	NaCl	0.38	74.36	2.27
	Na_2SO_4	0.11	91.51	3.46
1,3-Dichlorobenzene	No salt	3.77	27.35	2.18
	NaCl	0.81	57.86	3.78
	Na_2SO_4	0.55	68.97	4.46
1,4-Dichlorobenzene	No salt	5.05	21.93	3.09
	NaCl	1.04	51.62	3.80
	Na_2SO_4	0.72	62.77	3.93
1,2-Dichlorobenzene	No salt	7.77	15.44	2.22
	NaCl	1.33	45.38	3.85
	Na_2SO_4	0.91	57.45	4.41

Triplicate analyses
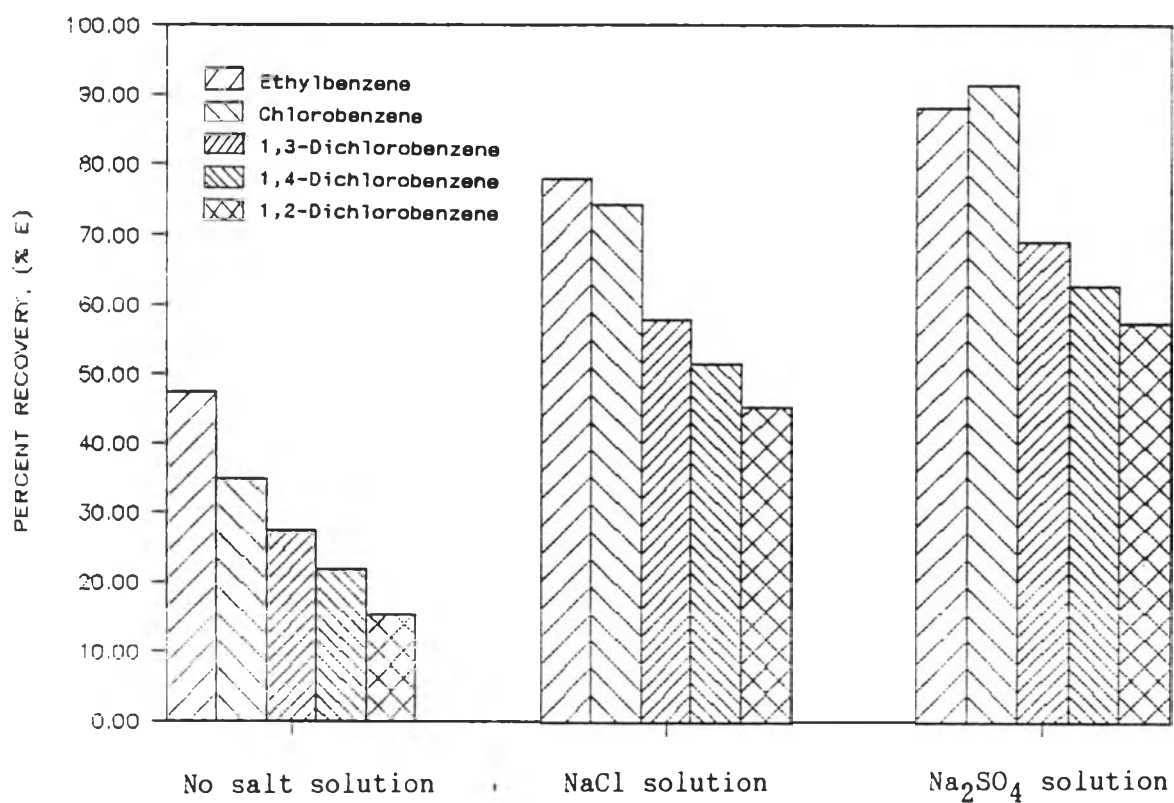
Figure 4.17 (a)   The effect of salting out on percent recovery of
each semivolatile organic compound at 50 ppb
in mixture solution.

Table 4.12   The results of salting out effect on percent recovery

of each semivolatile organic compounds in mixture

solution.

(b)   500   ppb standard solution

| Compound	Salt.	K	% E	%RSD
Ethylbenzene	No salt	1.68	45.24	2.53
	NaCl	0.32	76.80	0.43
	Na_2SO_4	0.22	84.45	4.00
Chlorobenzene	No salt	3.09	31.26	0.82
	NaCl	0.46	70.32	0.86
	Na_2SO_4	0.17	87.24	3.81
1,3-Dichlorobenzene	No salt	4.79	22.72	1.98
	NaCl	0.99	52.30	2.93
	Na_2SO_4	0.72	62.59	9.47
1,4-Dichlorobenzene	No salt	5.99	19.02	2.27
	NaCl	1.20	47.61	3.18
	Na_2SO_4	0.84	57.99	9.79
1,2-Dichlorobenzene	No salt	8.35	14.43	2.67
	NaCl	1.50	42.10	3.93
	Na_2SO_4	1.05	53.30	10.62

Triplicate analyses
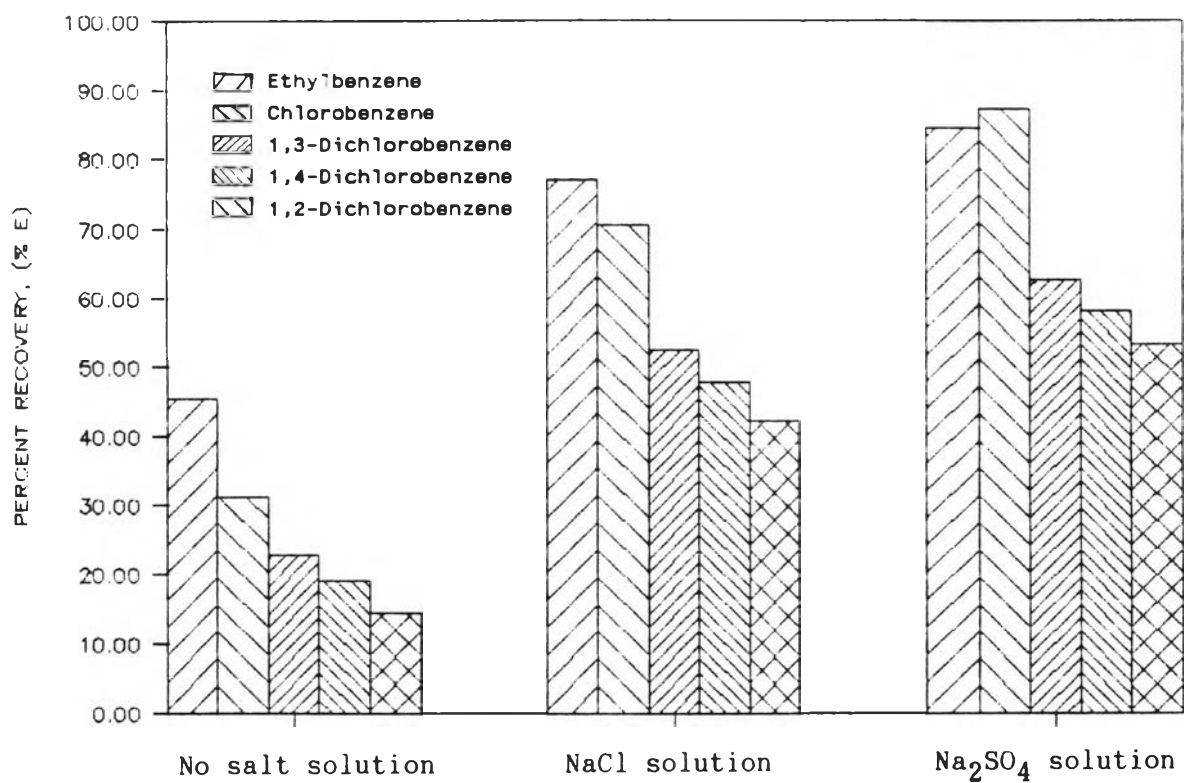
Figure 4.17 (b)   The effect of salting out on percent recovery of
each semivolatile organic compound at 500 ppb
in mixture solution.

According to the percent recoveries in Table 4.13, it is shown that the percent recovery of each semivolatile organic compound in single component or mixture solutions at the two different concentrations is insignificantly different. This indicates that the concentration does not have any effect on the percent recovery of each semivolatile organic compound.

Moreover, the data in Table 4.14 is demonstrated that the percent recovery of each semivolatile organic compound of single component solution is not much different from the percent recovery of each semivolatile organic compound in the mixture solution. Therefore, the percent recovery of an individual semivolatile organic compound at the two different concentrations is not affected by the presence of other organic compounds in the water samples.

Table 4.13   The percent recovery of each semivolatile organic
compound at two concentration levels of 50 ppb
and 500 ppb.

| Compound | Percent recovery, %E | | | |
| | Single component solution | | Mixture solution | |
	50 ppb	500 ppb	50 ppb	500 ppb
Ethylbenzene	47.56	42.99	47.35	45.24
Chlorobenzene	29.16	28.82	34.88	31.26
1,3-Dichlorobenzene	24.67	25.03	27.35	22.72
1,4-Dichlorobenzene	14.98	17.02	21.93	19.02
1,2-Dichlorobenzene	9.57	12.60	15.44	14.43

Triplicate analyses

Table 4.14   The percent recovery of each semivolatile organic

               compound in the single component solution and the

               mixture solution.

Compound*	Percent recovery, %E			
	50 ppb ini. Concn.		500 ppb ini. Concn.	
	Type of solution		Type of solution	
	single component	mixture	single component	mixture
ETB	47.56	47.35	42.99	45.24
CB	29.16	34.88	28.82	31.26
mCB	24.67	27.35	25.03	22.72
pCB	14.98	21.93	17.02	19.02
oCB	9.57	15.44	12.60	14.43

Triplicate analyses

* ETB = Ethylbenzene ,   CB = Chlorobenzene,

    mCB = 1,3-Dichlorobenzene,   pCB = 1,4-Dichlorobenzene

    oCB = 1,2-Dichlorobenzene

4.7 Minimum Detectable Level (MDL)

The minimum detectable level is defined as the smallest amount of solute required to produce a signal that is twice the noise level (61). The optimum headspace analysis condition used in the investigation of accuracy and analyses of the real water samples is shown in Table 4.15; and therefore, it is also used to determined the minimum detectable level of each semivolatile organic compound in aqueous solution under GC condition as described in Table 3.2. The results obtained from the study are presented in Table 4.16.

Table 4.15   The optimum headspace analysis condition used in the investigation of the accuracy and analyses of the real water samples.

Equilibration time	30 minutes
Temperature for equilibrating sample	45.0 $^{\circ}$C
Liquid to gas phases ratio	25:35
Injection volume	2.00 mL
Salt used	10.00 g of anhydrous Na_2SO_4

Table 4.16   The minimum detectable level of each semivolatile

organic compound in aqueous solution.

Semivolatile Organic Compound	Minimum Detectable Level (ppb)
Ethylbenzene	0.53
Chlorobenzene	0.48
1,3-Dichlorobenzene	0.99
1,4-Dichlorobenzene	1.00
1,2-Dichlorobenzene	0.98

4.8   The Accuracy of Headspace Analysis

The accuracy of headspace analysis technique is investigated by comparing the results of concentration of each semivolatile organic compound obtained from the analysis with the true concentration of each compound in synthetic unknown mixture solution. The unknown is prepared in methanol and it is diluted with distilled water prior to the analysis. The concentration of each semivolatile organic compound in the synthetic unknown solution is determined by means of external standardization method and standard addition method as described in section 3.8.1 and 3.8.2 , respectively.

The results obtained from the study are presented in Tables 4.17 - 4.18. The percent error in the determination of the concentration of each semivolatile organic compound in the synthetic unknown mixture is in the ranges of 0.04-11.63 % for the analysis

Table 4.17   The results of the analysis of synthetic unknown

solution by standard addition method.

Semivolatile	Concentration (ppb)		% Error
Organic Compound	True	Experiment	
Ethylbenzene	90.53	80.00	11.63
Chlorobenzene	75.10	75.07	0.04
1,3-Dichlorobenzene	60.03	64.63	7.66
1,4-Dichlorobenzene	20.92	22.38	6.98
1,2-Dichlorobenzene	89.87	92.01	2.38

Triplicate analyses

Table 4.18   The results of the analysis of synthetic unknown

solution by external standardization method.

Semivolatile	Concentration (ppb)		% Error
organic compound	True	Experiment	
Ethylbenzene	90.53	86.91	4.00
Chlorobenzene	75.10	75.63	0.71
1,3-Dichlorobenzene	60.03	60.95	1.53
1,4-Dichlorobenzene	20.92	22.09	5.59
1,2-Dichlorobenzene	89.87	84.50	5.98

Triplicate analyses

with standard addition method and is in the range of 0.71 - 5.98 % for the analysis with external standardization method.

All of the results obtained from the above studies indicate that the headspace analysis technique seems to be the best alternative method for the determination of semivolatile organic compounds in water samples. The reasons for this are that :

(a) This technique gives the good precision and good accuracy .

(b) It requires no preconcentration step for the determination of trace semivolatile organic compound in water .

(c) No interference peaks of uninterested nonvolatile organic compounds appear on the chromatogram, so the chromatographic analysis time is short.

(d) The minimum detection limit is found to be in the mid-ppb level using flame ionization detector.

(e) It is an economic method as shown in Table 4.19. The resons of this are that the septa, aluminum foils, aluminum caps and serum vials used in this technique can be purchased locally and also the price of the constant temperature water bath used in this study is cheaper than a commercial headspace sampler used in the conventional headspace analysis technique.

Table 4.19 The comparison of the price of materials used in the headspace technique developed in this study with the commercially available headspace sampler.

Item	Quantity	Price (U.S.$)
** Serum vials	36	7
* Serum vials	36	33
** Black rubber /aluminum foil septa	1000	1
* Teflon/rubber septa	1000	28
** Aluminum caps	1000	1.4
* Aluminum caps	1000	9
** Temperature water bath	1	600
* Headspace sampler option	1	13,000

** materials used in the developed headspace technique.

* materials used in the commercial headspace sampler.

4.9   The Determination of Semivolatile Organic Compound in Real Water Samples.

Three wastewater samples collected from three pools in the Chulalongkorn University are analyzed by the headspace analysis technique under the optimum headspace analysis condition as shown in Table 4.15 and under the GC condition as described in Table 3.2. The chromatograms of the unknown samples are shown in Figures 4.19 through 4.21 (a).

The retention times (t_r) of the unknown peaks obtained from the chromatogram of the unspiked samples are compared with the retention times of the standard semivolatile organic compounds mixture. The chromatogram of standard mixture solution is shown in Figure 4.18. It is found that sample #1 and sample #2 are not consisted of the interested compounds, and sample #3, however, seems to have chlorobenzene and 1,4-dichlorobenzene. To confirm this result, the sample #3 is spiked with the standard mixture solution in methanol and it is analyzed under the identical analysis conditions as the unspiked sample. The chromatograms of the unspiked sample #3 and the spiked sample #3 are shown in Figure 4.21(a) and Figure 4.21(b). It can be seen that the peak at t_r 4.34 min for unknown sample appears slightly different from the standard ethylbenzene peak (t_r 3.98 min) as shown in Figure 21 (b). However, the unknown peaks in Figure 4.21 (a) at t_r 6.61 min and t_r 14.64 min elute at the same time   as   the peaks of standard chlorobenzene (t_r 6.61 min) and standard 1,4-dichlobenzene (t_r 14.30 min), respectively as shown in Figure 4.21(b). Therefore, it seems to be that there are chlorobenzene and 1,4-dichlorobenzene in the sample #3.

Moreover, the sample #3 was rechecked by means of absolute retention time method with a different type of column, i.e., 2 m x 3 mm ID, stainless steel column packed with 5 % Di-isodecyl Phthalate (DIDP) on Chromosorb WAW, 60/80 mesh. The chromatograms of the sample #3 and the standard mixture in aqueous solution obtained from this column are shown in Figure 4.22(a) and Figure 4.22(b), respectively. From the result, it can be concluded that Chlorobenzene may be only one component in the sample #3 .

The components in the sample #3 is already identified and it is then quantified by standard addition method as described by the procedure in section 3.8.2 and the concentration of chlorobenzene in sample #3 is 0.60 ppb.
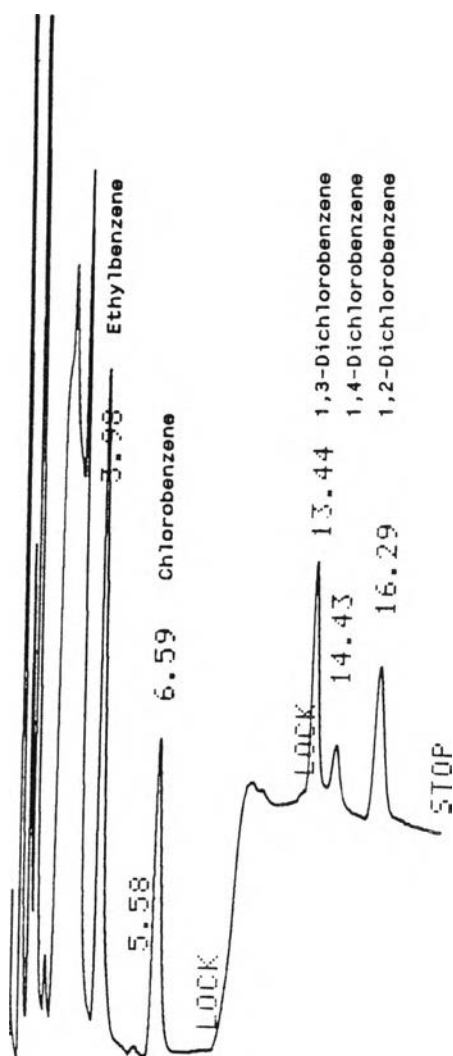
Figure 4.18   The gas chromatogram of standard mixture in

aqueous solution.

Condition : 1.8 m x 3 mm ID, glass column packed

with 8.9 % FFAP on chromosorb WAW, 100/120 mesh;

Oven temperature, hold at 80 $^{\circ}$C for 9 min, then

programmed at rate 30 ^{C}C/min and hold for 8 min;

Injection port temperature, 210 $^{\circ}$C;

Dectector, FID;   Dectector temperature, 210 $^{\circ}$C;

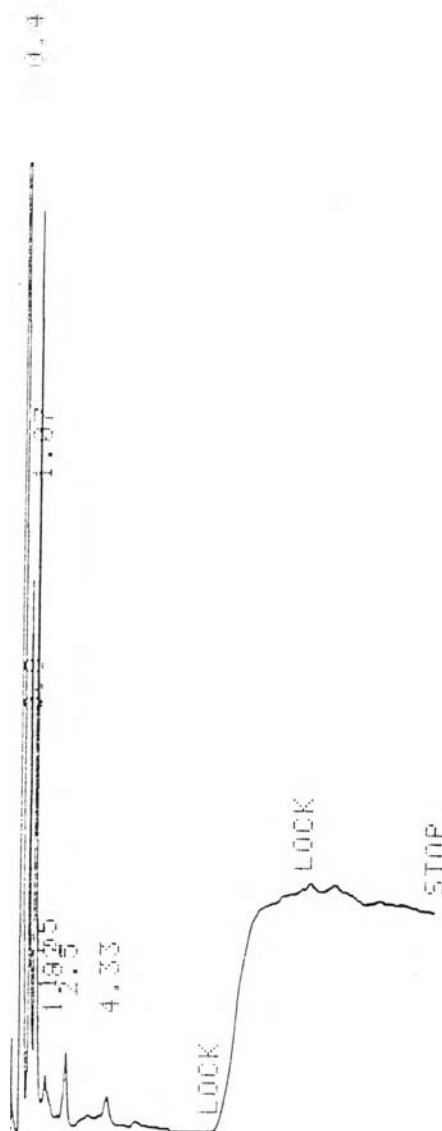Carrier gas, N_2 30 mL/min;   Sample Size, 2 mL.

Figure 4.19   The gas chromatogram of a real sample #1[*]

Condition : 1.8 m x 3 mm ID, glass column packed

with 8.9 % FFAP on chromosorb WAW, 100/120 mesh;

Oven temperature, hold at 80 $^{\circ}$C for 9 min, then

programmed at rate 30 $^{\circ}$C/min and hold for 8 min;

Injection port temperature, 210 $^{\circ}$C;

Dectector, FID; Dectector temperature, 210 $^{\circ}$C;

Carrier gas, N_2 30 mL/min; Sample Size, 2 mL.

[*] collected from the pond near the main gate by Phyathai Road of Chulalongkorn University.

Figure 4.20   The gas chromatogram of a real sample #2[*]

Condition : 1.8 m x 3 mm ID, glass column packed

with 8.9 % FFAP on chromosorb WAW, 100/120 mesh;

Oven temperature, hold at 80 ^{o}C for 9 min, then

programmed at rate 30 ^{o}C/min and hold for 8 min;

Injection port temperature, 210 ^{o}C;

Dectector, FID;   Dectector temperature, 210 ^{o}C;

Carrier gas, N_2 30 mL/min;   Sample Size, 2 mL.

[*] collected from the pool in fornt of the Chemistry Building 1,

Chulalongkorn University.

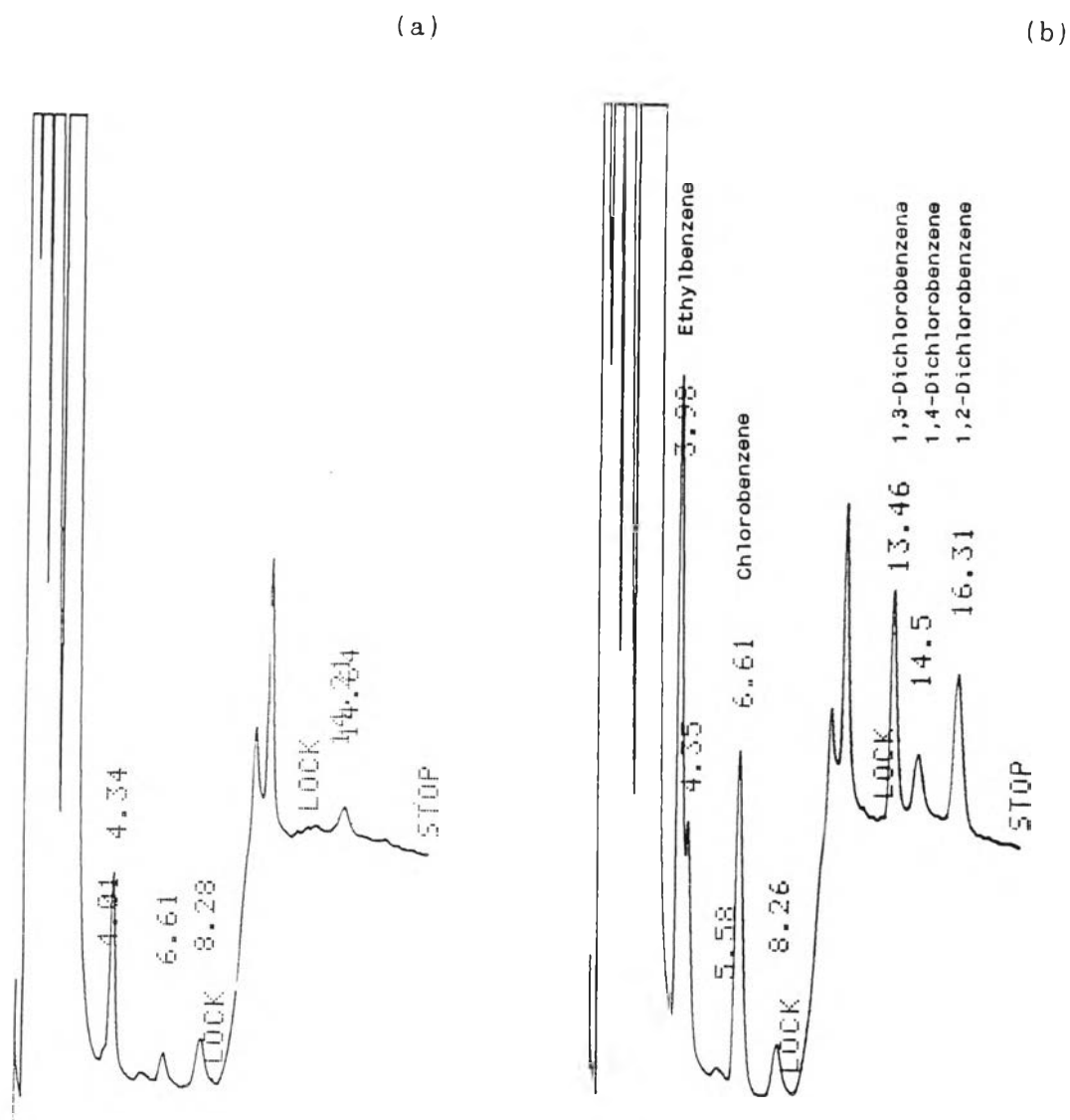(a)   (b)

Figure 4.21   The gas chromatogram of a real sample #3[*]

(a) unspiked sample, (b) spiked sample.

Condition : 1.8 m x 3 mm ID, glass column packed

with 8.9 % FFAP on chromosorb WAW, 100/120 mesh;

Oven temperature, hold at 80 ^{O}C for 9 min, then

programmed at rate 30 ^{O}C/min and hold for 8 min;

Injection port temperature, 210 ^{O}C;

Dectector, FID: Dectector temperature, 210 ^{O}C;

Carrier gas, N_2 30 mL/min;   Sample Size, 2 mL.

[*] collected from the pool behind the Chemistry Building 2,
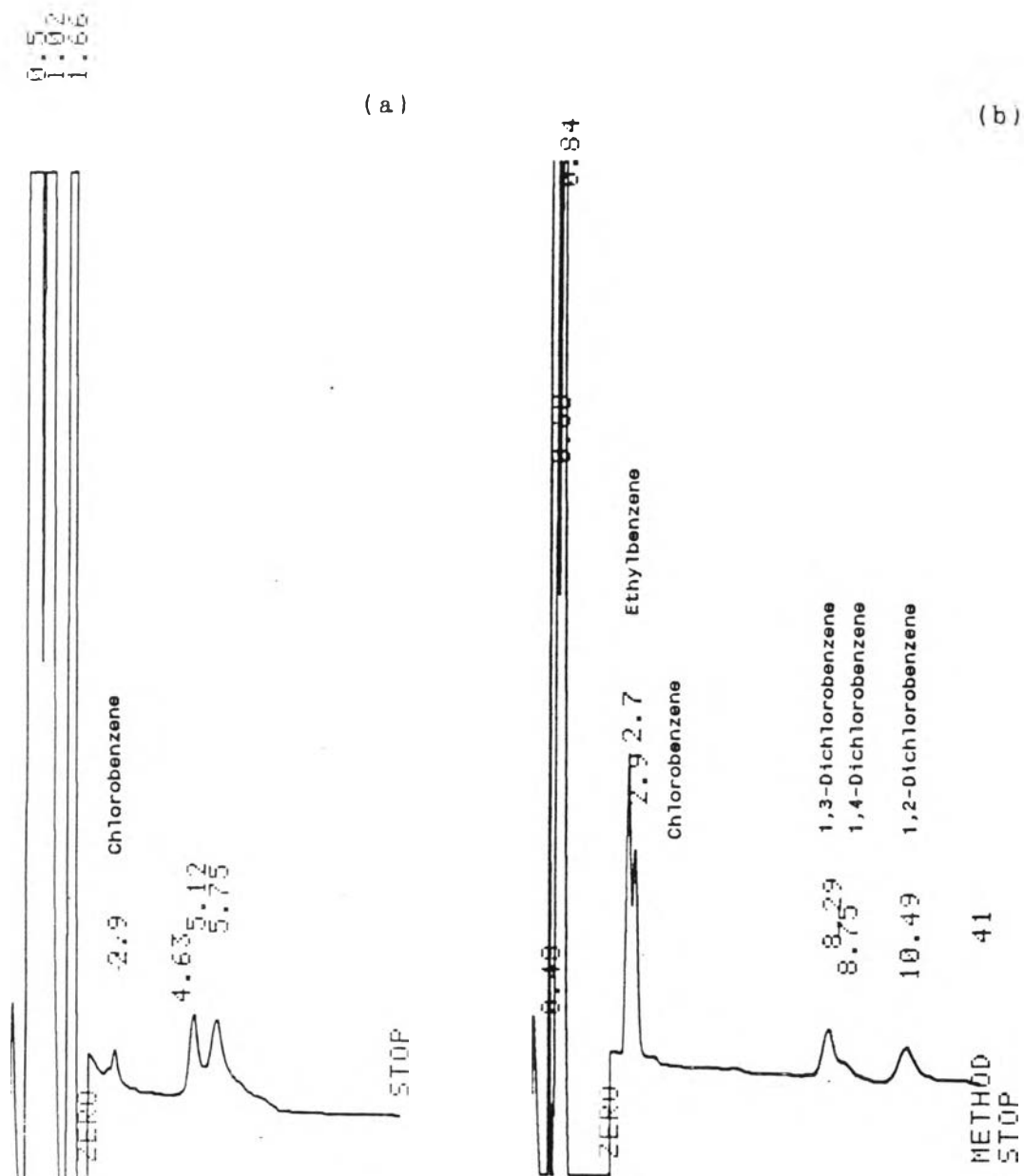
Chulalongkorn University.

Figure 4.22   The gas chromatogram of (a) real sample #3[*] ,

(b) standard mixture in aqueous solution.

Condition : 2 m x 3 ID, Stianless Steel column

packed with 5 % DIDP on chromosorb WAW,

60/80 mesh; Oven temperature, 100 ^{o}C ;

Injection port temperature, 210 ^{o}C;

Dectector, FID;   Dectector temperature, ?10 ^{o}C;

Carrier gas, N$_2$ 30 mL/min;   Sample Size, 2 mL.

[*] collected from the pool behind the Chemistry Building 2,

Chulalongkorn University.